

## The permeability of hydrogen in bulk palladium at elevated temperatures and pressures

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### Abstract

The permeability of hydrogen in bulk palladium membranes (approximately 1-mm thickness) was determined for the first time at conditions of simultaneously elevated temperature (623–1173 K) and hydrogen pressure ( $0.1 \times 10^6$  to  $2.76 \times 10^6$  Pa). When the hydrogen partial pressure exponent value was constrained to a value of 0.5, the permeability was described by an Arrhenius-type relation where the pre-exponential constant and activation energy for this correlation were  $1.92 \times 10^{-7}$  mol/(m s Pa<sup>0.50</sup>) and 13.81 kJ/mol, respectively. These Arrhenius values were in good agreement with prior low-pressure correlations.

However, the hydrogen flux results of this study were most accurately represented by an Arrhenius permeability expression where  $3.21 \times 10^{-8}$  mol/(m s Pa<sup>0.62</sup>), 13.41 kJ/mol, and 0.62 represent the pre-exponential constant, activation energy of permeation and permeability driving force, respectively. Although the partial pressure exponent value of 0.62 was slightly greater than the commonly accepted value of 0.5 (atmospheric and sub-atmospheric pressure studies), the optimal exponent value in this study decreased as the upper limit of pressure employed in the database was reduced. Therefore, the deviation in the partial pressure exponent with increasing hydrogen pressure may be attributed to variances in the product of the diffusion coefficient and Sieverts constant at elevated pressures.

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**Keywords:** Gas separations; Metal membranes; Palladium; Permeability

### 1. Introduction

There exists considerable interest today in the development of high-performance membranes for hydrogen-separation. Such membranes would have the potential for profound improvements in efficiency

for the separation and purification of hydrogen in applications ranging from gasification to fuels refining. For example, substantial advantages can be gained in operating the water-gas shift reaction at very high temperatures provided that the low equilibrium conversion of carbon monoxide can be enhanced by recovering a hydrogen permeate stream through use of a membrane reactor [1].

One particularly significant technical challenge is the development of hydrogen-separation membranes that can withstand severe operating conditions of

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**Nomenclature**

$C_H$	hydrogen atom concentration in metal (mol/m <sup>3</sup> )
$D_M$	diffusion coefficient of hydrogen atom in metal (m <sup>2</sup> /s)
$E$	activation energy for membrane permeability (J/mol)
$k$	hydrogen permeability of metal (mol/(m s Pa <sup>0.5</sup> ))
$k'$	hydrogen permeance of metal (mol/(m <sup>2</sup> s Pa <sup>0.5</sup> ))
$k_0$	hydrogen permeability constant (mol/(m s Pa <sup>0.5</sup> ))
$K_S$	Sieverts constant (mol/(m <sup>3</sup> Pa <sup>0.5</sup> ))
$n$	pressure exponent (0.5–1.0)
$N_H$	flux of hydrogen atoms (mol H/(m <sup>2</sup> s))
$N_{H_2}$	flux of hydrogen molecules (mol H <sub>2</sub> /(m <sup>2</sup> s))
$P$	total pressure (Pa)
$P_{H_2}$	hydrogen molecule partial pressure (Pa)
$P_{H_2,perm}$	hydrogen molecule partial pressure on permeate side (Pa)
$P_{H_2,ret}$	hydrogen molecule partial pressure on retentate side (Pa)
$R$	gas constant (8.314 J/(mol K))
$R^2$	the proportion of the variance in $y$ attributable to the variance in $x$
$T$	temperature (K)
$X_M$	membrane thickness (m)

elevated temperature and pressure. There is relatively little hydrogen permeability data at high-temperature, high-pressure conditions, even with materials such as palladium that have otherwise been studied extensively. Although its high cost, along with other factors such as the susceptibility to poisoning, precludes the use of pure bulk palladium as a practical hydrogen-separation membrane, composite membranes containing small amounts of palladium or palladium alloys are still of considerable interest. Therefore, it becomes important to understand the behavior of the bulk material at severe operating conditions. This paper describes a study of the permeability of bulk palladium

at temperatures up to 1173 K, and simultaneous application of hydrogen pressures to  $2.76 \times 10^6$  Pa.

### 1.1. Palladium as a membrane material

Palladium was first identified as a highly hydrogen-permeable material in the 19th century [2–4] and it is still used for high-performance hydrogen-separation applications today. Palladium has advantages over other membrane materials because of its catalytic surface, high hydrogen permeability, infinite hydrogen selectivity, temperature stability, and corrosion resistance. Palladium exhibits high catalytic activity for the adsorption and dissociation of hydrogen into atoms entering the membrane and recombination of the atoms into molecular hydrogen exiting the membrane. Diffusion of the hydrogen through the palladium is attributed to the “jumping” of hydrogen atoms through the octahedral interstitial sites of the face-centered cubic palladium lattice [5]. The lattice-diffusional mode of mass transfer for hydrogen results in the essentially infinite selectivity observed with dense palladium membranes. The hydrogen permeability of palladium increases with temperature because the endothermic activation energy for diffusion dominates the exothermic adsorption of hydrogen on palladium [6].

Palladium experiences an  $\alpha \rightarrow \beta$  phase transition at temperatures and hydrogen pressures below 568 K and 2000 kPa, respectively [7]. The lattice expands at the phase transition point increasing in volume by about 10%. This unit cell volume change can result in mechanical strains, physical distortions and possibly failure of the palladium if cycled through the palladium hydride phase transition region. The problem can be remedied by exposing the palladium to hydrogen only at temperatures above 568 K. Since the  $\beta$ -hydride is the only phase present at these conditions, palladium will not be subjected to the stresses caused by the phase transition.

### 1.2. Expressions for flux and permeability

The ability to transport hydrogen through palladium membranes is typically quantified in terms of permeability, permeance or flux. The *flux* of hydrogen through palladium is the product of the diffusion coefficient and the concentration gradient, with the

flux of hydrogen atoms being twice that of hydrogen molecules:

$$N_H = 2N_{H_2} = -D_M \frac{\Delta C_H}{X_M} \quad (1)$$

For thick membranes ( $X_M > 100 \mu\text{m}$ ), the limiting resistance is assumed to be the transport of hydrogen atoms through the palladium. Under these conditions, the surface reaction is considered to be very fast and the dissolved hydrogen atoms at the surface of the palladium are in equilibrium with the hydrogen gas on either side of the membrane. The concentration of hydrogen atoms in the palladium can be related to the hydrogen partial pressure via the *Sieverts equation*. The exponent of 0.5 reflects the dissociation of the gaseous hydrogen molecule into two hydrogen atoms that diffuse into the metal, where an ideal solution of hydrogen atoms in palladium is formed:

$$C_H = K_S P_{H_2}^{0.5} \quad (2)$$

Combining these expressions [8] yields the *Richardson's equation*:

$$N_{H_2} = -\frac{D_M K_S}{2} \frac{(P_{H_2, \text{ret}}^{0.5} - P_{H_2, \text{perm}}^{0.5})}{X_M} \quad (3)$$

The hydrogen *permeability* of the palladium corresponds to the constants in Eq. (3), or one half of the product of the diffusion coefficient and the *Sieverts constant*:

$$k = \frac{1}{2} D_M K_S \quad (4)$$

Therefore, the hydrogen flux is inversely proportional to the membrane thickness, and directly proportional to the product of the hydrogen permeability and the hydrogen partial pressure gradient across the membrane:

$$N_{H_2} = -k \frac{(P_{H_2, \text{ret}}^{0.5} - P_{H_2, \text{perm}}^{0.5})}{X_M} \quad (5)$$

Most prior investigations of unsupported, bulk palladium membranes ( $X_M > 100 \mu\text{m}$ ) have been expressed in terms of Eq. (5). Alternatively, an expression for flux can be derived as being proportional to the difference of the hydrogen partial pressure raised to an exponent with a value of ' $n$ ', as shown in Eq. (6):

$$N_{H_2} = -k \frac{(P_{H_2, \text{ret}}^n - P_{H_2, \text{perm}}^n)}{X_M} \quad (6)$$

One prior study of unsupported, bulk palladium membranes resulted in an ' $n$ ' value greater than 0.5. This study [9], which reported an ' $n$ ' value of 0.68, was the only investigation that employed high-pressure hydrogen on the feed side of the membrane (pressures up to  $0.71 \times 10^6 \text{ Pa}$ ).

The objective of the current study was to provide the first measurements of the hydrogen permeability of unsupported, bulk palladium at elevated temperatures (up to 1173 K) and pressures (up to  $2.76 \times 10^6 \text{ Pa}$ ). A membrane thickness of 1 mm was selected to minimize the influence of surface phenomena on the permeability results. Thinner ( $X_M < 100 \mu\text{m}$ ), supported membranes were not considered in this study because they exhibit permeability values and pressure exponents that differ significantly from bulk palladium. The permeability of these thinner palladium membranes are often not reproducible due to surface effects, leakage through defects in the thin palladium films, transport resistance of the substrate material, palladium surface contamination, palladium–support interface effects, flow of hydrogen across grain boundaries, thermal hysteresis, lattice dilatation or lattice defects [10,11].

## 2. Experimental

### 2.1. Membrane preparation

Membranes were fabricated by punching circular disks out of a 1-mm thick palladium sheet (Alfa Aesar, 99.99%). The palladium disks were polished using 800 grit silicon carbide paper prior to mounting into an Inconel 600-alloy holder. Two mounting methods were employed. In the first, a 16-mm diameter disk was mounted using a brazing technique developed at the National Energy Technology Laboratory (NETL). The brazing material was composed of high-purity gold powder with a boric acid flux which promoted braze flow and surface oxide removal. The mounted palladium membranes were heated to approximately 1473 K under an argon blanket for 5 min, and then permitted to cool to ambient temperature. The mounted membranes were then cleaned of flux contamination by boiling in deionized water for a minimum of 30 min. In the second method, a 19-mm diameter disk was welded directly between two pieces

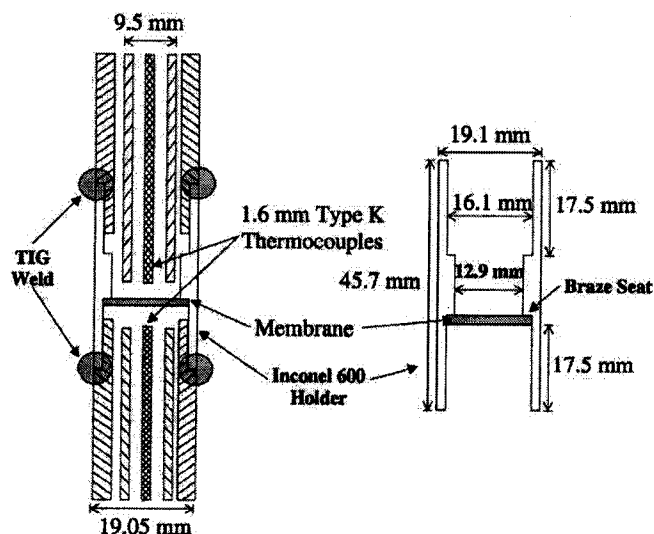


Fig. 1. Schematic of the palladium membrane set-up.

of Inconel 600 alloy tubing. No additional potential metal contaminants were introduced into the system with this latter method.

The mounted membrane, in its holder, was welded to predetermined lengths of 19.1 mm o.d. Inconel 600 tubing on both sides of the membrane holder assembly. These tubes acted as “extension tubes” and served to contain pressure and house components carrying feed gas and permeate gas both to and from the membrane. An example of the mounting configurations is illustrated in Fig. 1.

## 2.2. Permeability test unit

The hydrogen membrane testing (HMT) unit was designed and constructed at NETL [10,12]. The apparatus was designed to allow testing of inorganic hydrogen-separation membranes at simultaneously high temperatures and pressures, up to 1173 K and 3.1 MPa, respectively. A simplified schematic of the HMT unit is illustrated in Fig. 2. The membrane assembly consisted of two 9.5 mm o.d. Inconel 600 tubes, placed concentrically inside the 19.1 mm o.d. Inconel 600 extension tubes, approximately 6 mm from the membrane surface, as shown in Fig. 1. This coaxial tube configuration allowed the feed and sweep gases to enter through the annulus between the 19.1 and 9.5 mm o.d. tubes, contact the membrane, and exit

through the inside of the 9.5 mm o.d. tube. The membrane unit was heated by a Watlow 120 V, 150 mm long concentric resistance heater placed around the membrane assembly. The heater was controlled by an Iconic Genesis process control program and coaxially mounted type-K thermocouples, which were placed approximately 6 mm from the membrane surfaces. The membrane unit and resistance heater were insulated with ceramic fiber insulation and housed inside a 81 stainless steel containment vessel that was continuously purged with nitrogen. The containment vessel was used to ensure that any hydrogen escaping from the membrane apparatus would be diluted, cooled, and vented.

The membrane unit feed gas consisted of a mixture of 10% helium in hydrogen. Helium was used as an internal check for membrane leaks. Since helium cannot atomically permeate palladium, its detection in the permeate stream indicated a leak in the membrane or membrane-to-holder seal. The hydrogen–helium feed stream flow was maintained in the range of 190 to 250 sccm. An argon sweep gas was passed over the permeate side of the membrane at a rate that maintained the concentration of hydrogen in the permeate stream at less than 6 mol%. The feed and sweep gas flow rates were controlled by Brooks mass flow controllers. The process feed and sweep pressures were regulated by pneumatic, stainless steel

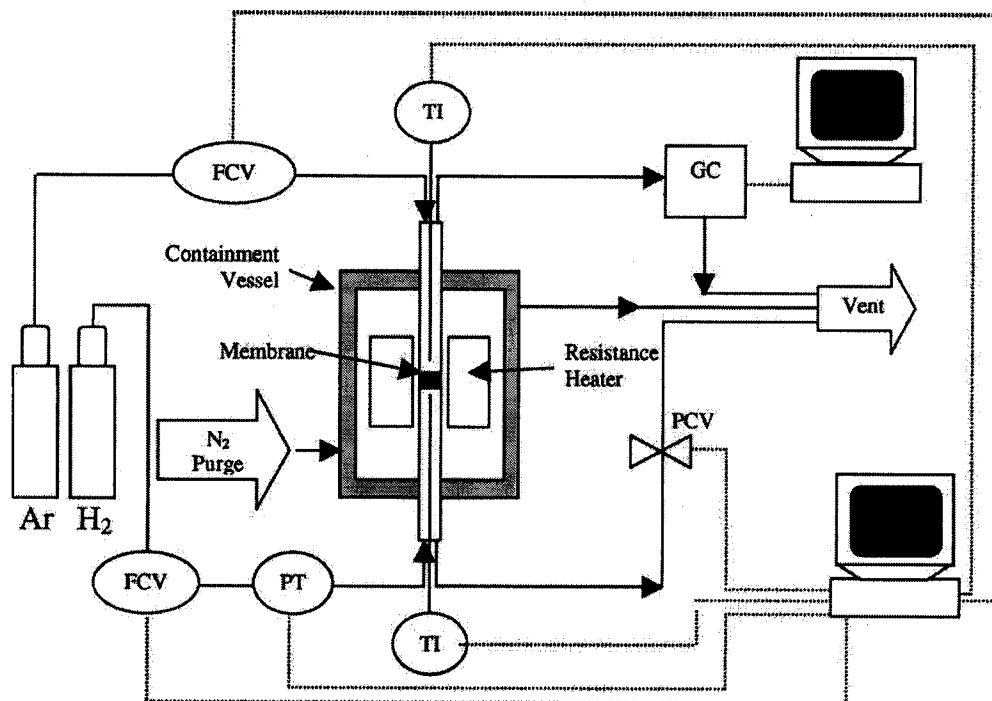


Fig. 2. Schematic of NETL's high-temperature, high-pressure hydrogen membrane testing (HMT) unit (FCV, flow control-valve; TI, temperature indicator; PCV, pressure control-valve).

Badger Research control-valves. In some cases, the sweep gas was maintained at atmospheric pressure, while in other cases, the sweep gas was pressurized to minimize the pressure drop across the membrane. Although data at lower temperature conditions were unaffected by the presence of a pressure drop, it was found that the palladium disk would deform under a large pressure gradient at the highest temperatures of interest (1038–1173 K). Therefore, the data taken in the absence of a pressure drop was deemed to be more reliable at these temperatures. The hydrogen-containing permeate stream was carried to a Hewlett Packard 5890 Series II gas chromatograph equipped with a 3.2 mm o.d., 3 m long, packed zeolite column and thermal conductivity detector for quantification.

### 3. Results and discussion

Hydrogen flux through three braze-mounted palladium membranes and three welded palladium

membranes was measured at temperatures and pressures ranging from 623 to 1173 K and  $0.1 \times 10^6$  to  $2.76 \times 10^6$  Pa, respectively. No discernable difference in data was found between the two mounting techniques. However, the palladium disks were found to physically deform under conditions of high-pressure drop at temperatures of 1037 and 1173 K. Data that were biased by membrane deformation were excluded from the permeability analysis. The results shown in Fig. 3 correspond to a pressure exponent value that was constrained to 0.5. Linear regression analysis of the five isotherms yielded  $R^2$  values ranging between 0.935 and 0.990, with an average value of 0.963.

Hydrogen permeability of the palladium membranes was determined at each temperature from the slope of these isotherms (Eq. (5)). The temperature dependence of the permeability values was then fit with an Arrhenius-type relation, Eq. (7):

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (7)$$

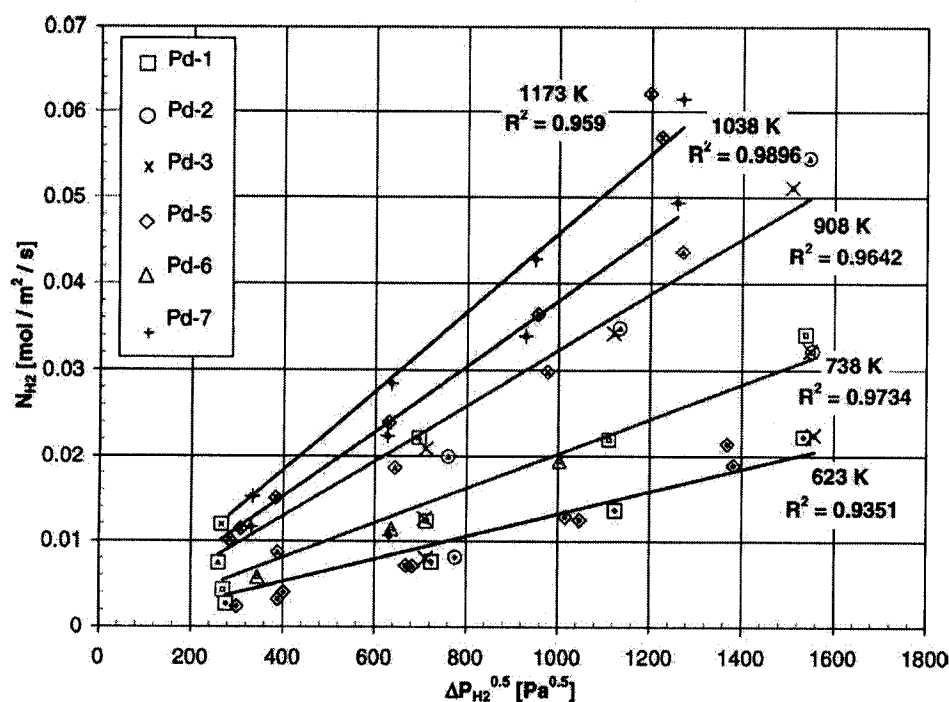


Fig. 3. Hydrogen permeability results with the partial pressure driving force exponent, 'n', constrained to 0.50.

The Arrhenius expression for the permeability of palladium, constrained to a hydrogen partial pressure exponent value of 0.5, was found to be

$$k \text{ (mol H}_2\text{/(m s Pa}^{0.5}\text{))} \\ = 1.92 \times 10^{-7} \exp \left\{ -\frac{13,810 \text{ (J/mol)}}{8.314 \text{ (J/mol K)} \times T \text{ (K)}} \right\} \quad (8)$$

An improved fit of the data was obtained by determining the optimal value of the hydrogen partial pressure exponent, 'n'. Fig. 4 illustrates the results for  $n = 0.62$ , the exponent value that optimized the average  $R^2$  value of the linear regression to 0.982.

The expression for hydrogen flux under this condition is

$$N_{H_2} \text{ (mol H}_2\text{/(m}^2\text{ s))} \\ = \frac{k(P_{H_2,ret}^{0.62} - P_{H_2,perm}^{0.62}) \text{ (Pa}^{0.62}\text{)}}{X_M \text{ (m)}} \quad (9)$$

Permeability values were determined from the slopes of best-fit isotherms in Fig. 4. The Arrhenius

expression that correlates these results is given in Eq. (10):

$$k \text{ (mol H}_2\text{/(m s Pa}^{0.62}\text{))} \\ = 3.21 \times 10^{-8} \exp \left\{ -\frac{13,410 \text{ (J/mol)}}{8.314 \text{ (J/mol K)} \times T \text{ (K)}} \right\} \quad (10)$$

X-ray photoelectric spectroscopy (XPS) analysis was conducted on a braze-mounted palladium membrane sample to diminish concerns of surface contamination by gold braze migrating onto the active transport area of the membrane surface, which may have manifested itself during exposures at elevated temperatures. The XPS analysis was conducted at three positions on the membrane surface—near the edge, midway and center. No evidence of gold was detected at the analyzed locations.

Many investigators have studied the permeability of unsupported, bulk palladium membranes with thicknesses in the 100 to 12,000  $\mu\text{m}$  range. Their experimental test conditions and permeability results are provided in Table 1 [9,13–18], along with the results

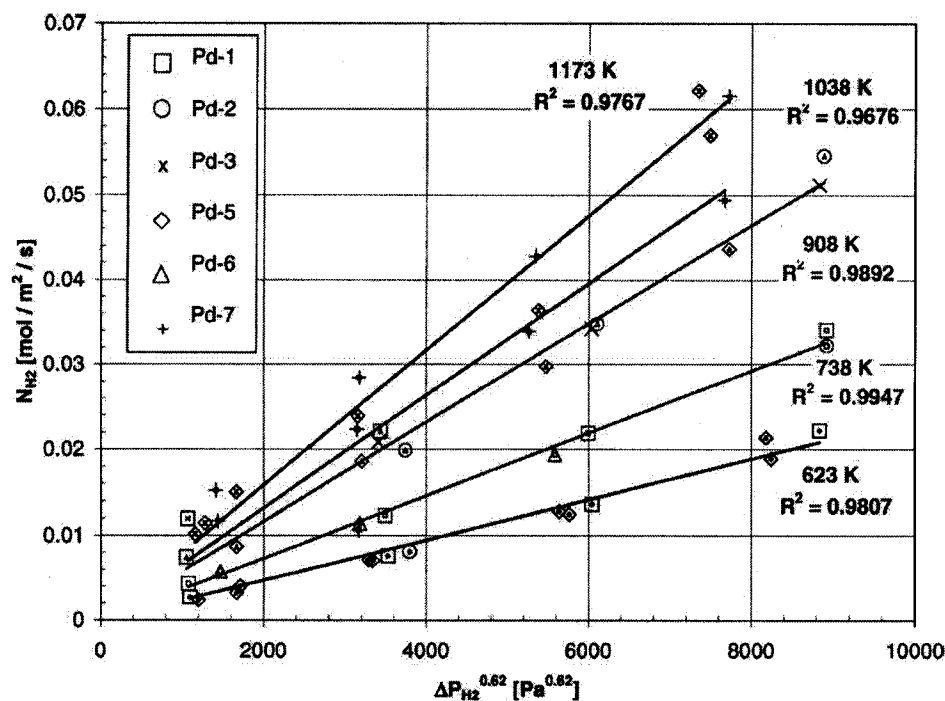


Fig. 4. Hydrogen permeability results with the best partial pressure representation ( $n = 0.62$ ) for the membranes and experimental conditions of this study.

of this study. These prior investigators, with a single exception, employed a high-vacuum test apparatus operating at sub-atmospheric hydrogen test pressures. These investigations reported a pressure exponent of 0.5 in the flux expression (Eq. (5)), as would be expected for bulk-diffusion controlled transport. Each investigation also described the temperature-dependence of the permeability values with an Arrhenius-type relation (Eq. (7)).

The temperature dependence of both the literature and NETL permeability values is shown in Fig. 5. This figure also illustrates how differences in the partial pressure driving force exponent,  $n$ , affect the reported permeability. The NETL expression for permeability is in good agreement with prior literature, provided that ' $n$ ' is constrained to a value of 0.5. The activation energy, 13.81 kJ/mol, and the pre-exponential factor,  $1.92 \times 10^{-7} \text{ mol H}_2/(\text{m s Pa}^{0.5})$ , fall well within the range of previously reported values listed in Table 1. It should be noted that when the partial pressure exponent ( $n$ ) is changed from 0.5 to the optimized to a value of 0.62, the units of measure associated with permeability cause a dramatic change

in its apparent value, Fig. 5. Additionally, the only prior high-pressure permeability results [9] illustrate similar effects to the partial pressure exponent as comparable to those reported in this high-pressure study.

Values of ' $n$ ' greater than 0.5 are commonly reported in ultra-thin, supported palladium membrane studies [10,11], where it is possible that the validity of the diffusion limited hydrogen transport mechanism assumption is debatable. An exponent value of 0.5 is indicative of the hydrogen atoms forming an ideal solution in palladium, thus leading to a diffusion limited transport mechanism, while a partial pressure exponent value approaching unity indicates a surface adsorption/dissociation or gaseous diffusion process is limiting. Partial pressure exponent values in the range of 0.5 and 1.0 may be attributable to a combination of a more complex transport mechanism involving both surface effects entering and exiting the membrane as well as the hydrogen diffusion process. Experiments described in this study were conducted with relatively thick palladium membranes ( $X_M \sim 1 \text{ mm}$ ). Therefore, an attempt was made to establish that the partial

Table 1  
Summary of published data for hydrogen permeability of bulk palladium membranes

	Davis [13]	Toda [14]	Hurlbert and Konecny [9]	Koffler et al. [16]	Holleck [15]	Balovnev [17]	Katsuta et al. [18]	NETL <sup>a</sup> ( $n = 0.5$ )	NETL <sup>b</sup> ( $n = 0.62$ )
$X_M$ ( $\mu\text{m}$ )	130–729	11,500	10–150	486–762	800–2025	100–1000	940	1000	1000
$T$ (K)	473–973	443–563	623–773	300–709	500–900	370–900	769–1219	623–1173	623–1173
$P_{\text{tot,ret}}$ (kPa)	$3 \times 10^{-3}$ –101	84–85	101–710	$4 \times 10^{-5}$ – $7 \times 10^{-3}$	53–54	$3 \times 10^{-8}$ – $7 \times 10^{-5}$	101	101–2757	101–2757
$P_{\text{H}_2,\text{ret}}$ (kPa)	$3 \times 10^{-3}$ –101	84–85	101–710	$4 \times 10^{-5}$ – $7 \times 10^{-3}$	53–54	$3 \times 10^{-8}$ – $7 \times 10^{-5}$	101	91–2480	91–2480
$P_{\text{tot,perm}}$ (kPa)	Vacuum	Vacuum	Vacuum	$1.3 \times 10^{-8}$	0.024–0.006	101.3	Vacuum	118	118
$P_{\text{H}_2,\text{perm}}$ (kPa)	Vacuum	Vacuum	Vacuum	$1.3 \times 10^{-8}$	0.024–0.006	1.3–10	Vacuum	Ar sweep	Ar sweep
$n$	0.5	0.5	0.68	0.5	0.5	0.5	0.5	0.5	0.62
$k_0$ ( $\text{mol}/(\text{m s Pa}^n)$ )	$3.85 \times 10^{-7}$	$1.72 \times 10^{-7}$	$1.47 \times 10^{-8}$	$2.2 \times 10^{-7}$	$1.42 \times 10^{-7}$	$1.89 \times 10^{-7}$	$3.82 \times 10^{-7}$	$3.31 \times 10^{-7}$	$5.65 \times 10^{-8}$
$E$ (kJ/mol)	18.56	13.46	11.92	15.67	12.81	15.46	20.50	13.81	13.41
Geometry	Disk	Wire	Disk	Disk	Disk	Disk	Disk	Disk	Disk

<sup>a</sup> The NETL data ( $n = 0.5$ ) yielded a  $R^2$  value of 0.963.

<sup>b</sup> The NETL data ( $n = 0.62$ ) yielded a  $R^2$  value of 0.982.



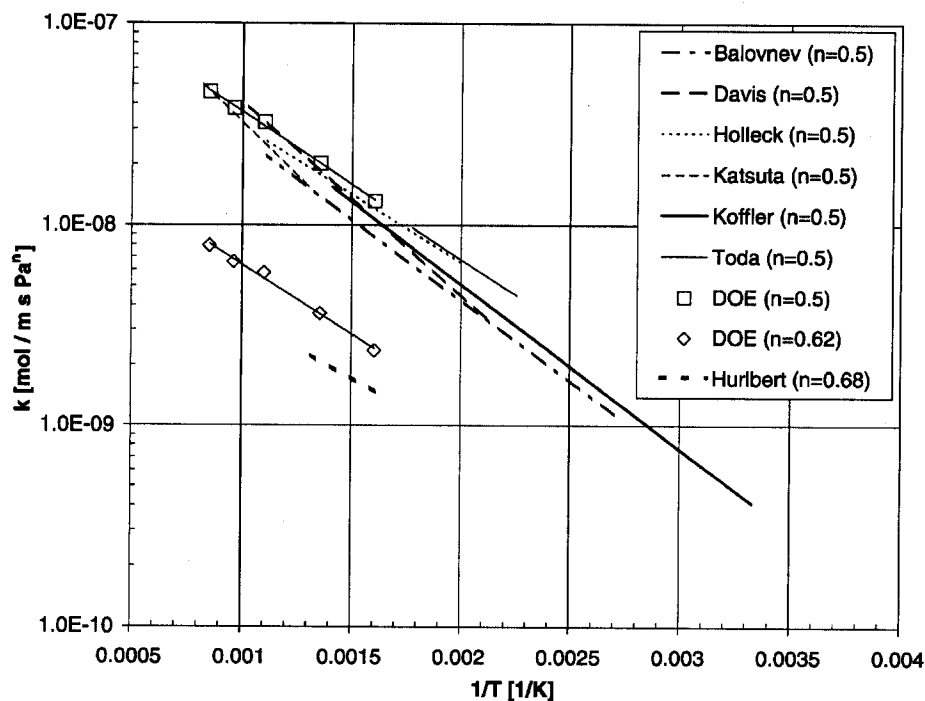


Fig. 5. Arrhenius comparison of literature palladium permeability values as a function of temperature and the results obtained in this study with the best representation ( $n = 0.62$ ) and constrained partial pressure exponent ( $n = 0.5$ ).

pressure exponent was a function of the increased hydrogen pressures associated with the high-pressure conditions of this study.

The optimal values of ' $n$ ' were determined as a function of the maximum pressure of the database used in analysis. Optimal values of ' $n$ ' were determined for the 0–175, 0–775, 0–1600 and 0–2600 kPa hydrogen pressure ranges. Fig. 6 illustrates that, in general, as the maximum pressure value decreased, the pressure effects were diminished and the optimized partial pressure exponent decreased. An extrapolation of these results to zero pressure indicated that the exponent approaches 0.53, which is close to the limiting value of 0.5 for bulk-diffusion controlled transport in bulk membranes at low-pressure.

A plausible cause for the relation between the retentate hydrogen pressure and the partial pressure exponent is the dependence of the permeability on the hydrogen concentration. The membrane permeability is proportional to the product of the solubility and diffusivity of the hydrogen/palladium system, Eq. (4). Thus, any changes in either of these values for the hydrogen/palladium system could account for an

increase or decrease in permeability. The diffusion coefficient of the palladium–hydrogen system has been shown to increase with increasing partial pressure [15] under sub-atmospheric studies, thus possibly increasing the membrane permeability. It has also been suggested that the diffusivity may actually decrease with pressure as the nearest neighbor sites for hydrogen atom jumps become filled [6]. A distinct trend between pressure and diffusivity could not be established in a comprehensive literature review of diffusivity data [5].

It is likely that the Sieverts constant would also have been influenced by high-pressure. It has been postulated that an increased concentration of hydrogen atoms within palladium form a non-ideal solution in which the dissolved hydrogen atoms exhibit attractive forces towards one another [6]. Such an effect would result in a concentration of hydrogen atoms greater than that predicted by a Sieverts constant based on low-pressure solubility data [5]. In this circumstance, the Sieverts constant for hydrogen-palladium would increase with increasing pressure over the range of pressure conditions examined. Thus, the product of the Sieverts constant and the diffusion coefficient of the

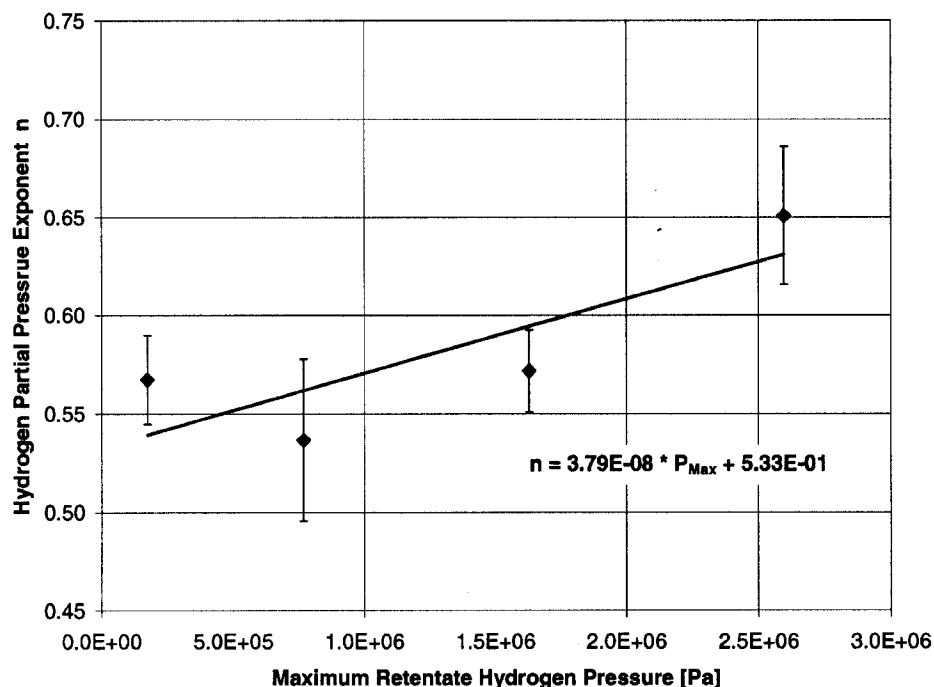


Fig. 6. The effect of the hydrogen feed pressure on partial pressure exponent, ' $n$ '. Error bars indicate range of ' $n$ ' values obtained from individual membrane tests, while points indicate average ' $n$ ' value from all membranes.

palladium–hydrogen system may be increasing with hydrogen pressures, resulting in increases in the membrane permeability. If the permeability, as defined as ' $k$ ' in Eq. (6), is held constant, the net mathematical effect becomes an increase in the partial pressure exponent with increasing hydrogen pressure.

The extent of the effects of increased pressure on the diffusion coefficient and solubility can not be differentiated using the data in this study. However, the net effect of increasing pressure on permeability can be ascertained through the observation that the flux data is consistently greater than expected for the "best-fit" permeability, Figs. 3, 4 and 6. This can only be explained by an increase in the product of the diffusion coefficient and the solubility with increases in hydrogen pressure.

#### 4. Conclusions

The permeability of hydrogen in bulk palladium was determined for the first time at the elevated temperature and pressure conditions associated with

gasifier and/or other process streams that are being considered as candidate feeds for membrane applications. The permeability results were comparable to those reported at lower pressures when the hydrogen partial pressure exponent of the hydrogen flux was constrained to a value of 0.5. A much better fit of the data was realized when the hydrogen partial pressure exponent value was optimized to a value of 0.62. This result was similar to a previously reported exponent value of 0.68 at 623 K [9]. The increase of the exponent value from 0.5 to 0.62 for the high-pressure study may be attributed to an invalid assumption of a diffusion-limited mechanism and/or changes in the Sieverts constant and diffusion coefficient with increasing pressure. Further research is required to separate the effects of solubility and diffusivity on the permeability at conditions of elevated pressure.

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